An Anomalous Breccia Associated with the Serpent Mound Impact Crater, Southern Ohio

Keith A. Milam[1] and Adam Hester, Department of Geological Sciences, and Peter Malinski, Department of Chemistry and Biochemistry, all of Ohio University, Athens, OH

Abstract. An anomalous carbonate breccia in the Serpent Mound impact crater in southwestern Ohio was examined and possible depositional/emplacement mechanisms were evaluated in an effort to determine its origin. This breccia was likely formed by sedimentary deposition and subsequent weathering during the Middle-Late Silurian prior to the Serpent Mound impact event. This origin is supported by the lateral extent of the breccia, the elevation range over which it is exposed, its spatial association with Middle-Upper Silurian strata, a mineral assemblage limited to dolomite, compositional homogeneity, and its similarity to Middle-Upper Silurian geologic units. Field observations, mineralogy, and geochemical analyses do not support emplacement by fault comminution, gravitational collapse of crater slopes, or ballistic/resurge deposition of ejecta.

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INTRODUCTION

The Serpent Mound Impact Crater

The Serpent Mound impact structure (which shares its name with the well-known Paleo-Indian effigy; Willoughby 1919) is a seven to eight km diameter (Reidel 1975; Reidel and others 1982) circular feature situated in southern Ohio at the junction of Adams, Highland, and Pike Counties (Fig. 1). The structure lies within the Bluegrass Section of the Interior Low Plateau physiographic province along the western edge of the Appalachian Plateau, known as the Allegheny Escarpment, and to the east of the Central Lowlands of western Ohio (Brockman 1998).

Although area bedrock consists of normally flat-lying Ordovician-Mississippian sedimentary rocks (Fig. 2), the Serpent Mound structure is a zone in which these strata have been disturbed. This was first described by Locke (1838) and later interpreted by Bucher (1933) and Reidel (1975) to have resulted from "cryptovolcanism" or a "cryptoexplosion". The absence of surface or subsurface igneous rocks and the lack of a volcanic root at depth discredit this notion (Bull and others 1967).

The Serpent Mound impact structure is the only known impact crater in the state of Ohio (Fig. 1). Its impact origin was confirmed with the discovery of shatter cones (Dietz 1960), shocked quartz (Carlton and others 1998; Koeberl and others 1998), and coesite (Cohen and others 1961) and is supported by the enrichment of siderophile elements at the center of the structure (Carlton and others 1998; Koeberl and others 1998). Serpent Mound represents the eroded remnant of a complex impact crater. Initial mapping efforts identified a centrally-uplifted area of Ordovician rocks surrounded by a circular graben of downward-displaced Devonian to Mississippian strata separated by a so-called "transition zone" (Fig. 1; Reidel 1975; Reidel and others 1982). The transition zone was characterized by Reidel (1975) and Reidel and others (1982) as an area of folded and faulted (primarily Silurian) strata not significantly displaced from normal positions. Carbonate breccia in this zone is the focus of this study.

An Anomalous Breccia in the Crater

The first descriptions of this anomalous breccia were made circa 1916 by August Foerste and Raymond Lamborn who identified this breccia as "marl" dividing the Silurian Bisher and Lilley Members of the (then) West Union Formation (Schumacher 2002c). Their field investigations identified at least 17 locations of the marl associated with the structure. Others (Stout 1940, 1941; Schmidt and others 1961) offered a contrasting view by attributing this unit to extensive weathering of the upper few meters of the Peebles Dolomite. Stout (1940) and Stout (1941) observed that the breccia was confined to Adams, Highland, and Pike Counties in southern Ohio. Stout (1941) further observed that it occurs in areas where strata between the Peebles Dolomite and Ohio Shale were absent. An impact origin for the breccia was suggested by

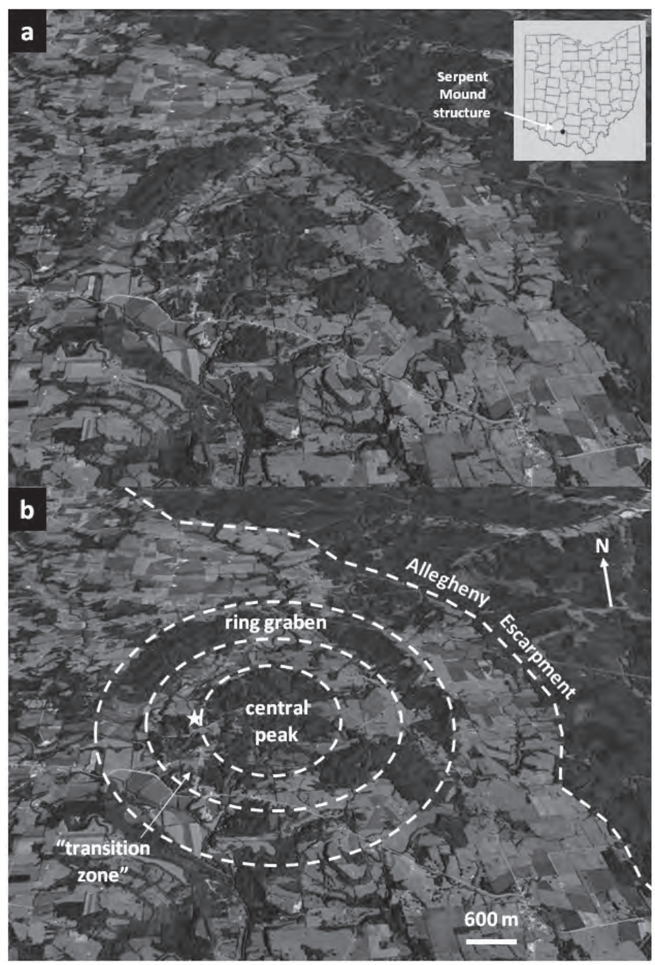


Figure 1. Oblique aerial views (looking to the NNE) towards the Serpent Mound impact structure (Google Earth/USDA Farm Service Agency). The inset box in (a) shows the location of the structure at the junction of Adams, Highland, and Pike Counties, while (b) shows the approximate outlines (dashed lines) of the major features within the crater as well as the breccia type location (star symbol).

[1]Address correspondence to Keith A. Milam, 213 Clippinger Laboatories, Athens, OH 45701. Email: milamk@ohio.edu

Dietz (1960) who reported "a quarry which revealed a large mass of what may be explosion breccia."

The breccia was first observed by the authors at a location, here designated the type location(Figs. 1, 3a, 4a) directly west of the central peak of the impact crater (39° 2.036"N, 83° 25.373" W). Later the search was expanded to include other parts of the impact crater (see Figs. 3-4 and below) and outside the limits of the disturbance as defined by Reidel (1975). The breccia ranges from matrix- to clast-supported and (apparently) polymict to monomict within and among exposures (Fig. 5). Clasts range from angular to sub-angular coarse sand to boulders and typically consist of massive or cross-bedded dolomicrite and algal mats. Most commonly the breccia is massively bedded, although poorly-developed bedding can be discerned at a few locales. At the type location (Fig. 3a) and at two other sites in the northern part of crater (Fig. 3, b and c), breccia exposures appear to display an overall fining upward sequence. Physical properties (hardness and reactivity to acid) indicated a carbonate composition for the breccia. Our initial observations and those of Stout (1940) and Stout (1941) support the notion that this breccia is not common to the local stratigraphy and may be confined to the Serpent Mound impact crater. Therefore deposition/emplacement of the breccia may be related to the crater landform and/or the impact event.

We test the four most plausible mechanisms for emplacement or deposition of the anomalous breccia: (1) pre-impact sedimentary deposition (and subsequent weathering), (2) comminution during fault movement, (3) gravitational collapse of the central peak, or (4) fallback/resurge of impact ejecta. As noted by earlier workers, the breccia may represent either the Middle Silurian Lilley or Bisher Formations (Schumacher 2002c) or simply a highly-weathered horizon of the Middle Silurian Peebles Dolomite (Schmidt and others 1961). As such, breccia should be found spatially associated with Middle Silurian units and its mineralogy and bulk composition should correlate most closely with Middle Silurian geologic units.

Period	Formation Name	Thickness (m)	Range of Elevations of Base (m)
Lower Mississippian	Cuyahoga Formation	15-98	329-366
	Sunbury Shale	3-15	341-366
	Berea Sandstone	3-15	366
	Bedford Shale	24-30	256-347
Upper Devonian	Ohio Shale	76-152	280
	Olentangy Shale	6-17	189-287
Upper Silurian	Tymochtee Formation	0-15	262
	Greenfield Dolomite	0-30	
Middle Silurian	Peebles Dolomite	12-21	247-277
	Lilley Formation	5.5-24	250-262
	Bisher Formation	6-26	219-256
	Rochester/Estill Shale	9-55	202-250
	Dayton Formation	0.6-2	201-238
Lower Silurian	Noland Formation	0-30	
	Brassfield Limestone	1.5-3	
Upper Ordovician	Drakes Formation	6-9	700
	Bull Fork/Waynesville Formation	27-37	61

Figure 2. Simplified stratigraphic column of rocks commonly exposed in the Serpent Mound area using thickness and elevation data from Rexroad and others (1965), Swinford (1985), Swinford (1991), Schumacher and Reidel (1997), Shrake and others (2007), Schumacher and Reidel (2002a), Schumacher (2002b), and Baranoski and others (2003).

Breccias produced by fault movements are common to impact craters (French 1998). The type location of the breccia is in the transition zone (Fig. 1) in an area where Reidel (1975) mapped numerous converging faults (Fig. 3). Faults cut across sedimentary strata ranging in age from the Lower Silurian Rochester (Estill) Shale to the Upper Devonian Ohio Shale (Fig. 2; Reidel 1975). Fault breccia, if present, should be exposed only in fault zones and its composition should represent a mixture of Lower Silurian to Upper Devonian strata.

Central peaks in complex craters are comprised of densely fractured and faulted crater floor strata that have been uplifted well above their normal stratigraphic positions (Grieve and Thierriault 2004). Following the rise of a central peak, this weakened material is particularly susceptible to gravitational collapse. The Serpent Mound central peak is comprised of Upper Ordovician –Middle Silurian carbonates and shales (Reidel 1975). If the anomalous breccia is the product of gravitational collapse, then it should be only locally exposed along the flanks of the central peak and represent a compositional mixture of Upper Ordovician-Middle Silurian target rocks (Fig. 2). However, if the collapse was more recent, then the breccia should represent a mixture of geologic units to the nearby eastern drainage divide for the type location, consisting of strata from the Lower Silurian Brassfield Limestone to the dolostones of the Middle Silurian (Fig. 2).

Breccias (lithic or melt) are commonly found in, near, or associated with terrestrial impact craters (French 1998), deposited following fragmentation and ejection of material (ejecta) from an impact event. Most are deposited immediately adjacent to or away from the crater rim, whereas some is entrained in the impact plume and settles on the crater floor. In shallow marine settings, where an impactor excavates and ejects both seawater and the ocean floor, collapse of the transient cavity results in resurge of the excavated water column. This resurge also entrains and deposits ejecta on the crater floor (e.g. Ormö and Lindström 2000; Dypvik and Jansa 2003).

If the anomalous breccia represents impact ejecta, then it would represent a mixture of strata ejected during the Serpent Mound impact event. The typical excavation depth for impact craters is approximately one-tenth of the transient crater diameter (Melosh 1989), a parameter not directly measureable in complex craters whose rims have characteristically collapsed. However, impact modeling has shown that the transient crater diameter (D_t) is approximately 50-60 percent of the final crater diameter (D_f) (Melosh 1989). With a maximum diameter of eight km (Reidel 1975), the D_t for Serpent Mound would have ranged from 4.0-4.8 km. Therefore the estimated excavation depth ranged from 400-480 m. A Late Mississippian impact would have excavated to a depth that exceeds the total thickness of the Upper Ordovician-Lower Mississippian carbonate-rich sedimentary strata still exposed near the impact site. A Pennsylvanian-Permian impact (a possibility offered by Watts 2004) would have excavated additional siliciclastic sedimentary strata no longer preserved at the crater.

METHODS

This study seeks to determine which of the mechanisms were responsible for the deposition or emplacement of the breccia. Field observations, mineralogical, and geochemical analyses were employed to assess each of the four geologic processes.

In an effort to determine the occurrence and lateral distribution of the anomalous breccia in the Serpent Mound impact structure, we systematically revisited purported marl and breccia sites as first identified by Foerste and Lamborn (Schumacher 2002c) and Reidel (1975). Exposures were observed and described and samples were collected and compared to the type location to confirm the presence of the anomalous breccia elsewhere. The latitude, longitude, and elevation of each confirmed site were measured with a Garmin Colorado 400t GPS receiver [~5 m and ~3 m horizontal (WGS 84) and vertical (NAD27) accuracy respectively,] and results were plotted on a geologic map of the structure (Fig. 3). Our team also systematically searched both inside and outside of the crater (outer limits defined by Reidel 1975) for additional breccia exposures.

To assess which of the locally-exposed geologic units might comprise the anomalous breccia, 22 samples of undisturbed geologic units from outside of the crater and 13 samples of the anomalous breccia were collected, described, and processed for geochemical analyses (Table 1). Between 10-20 g of each sample (including both clasts and matrix) was ground into powder (clay-size) using an agate mortar and pestle, mixed thoroughly, and separated into three aliquots. The first two aliquots (4-8 g each) were used for geochemical analyses, while the remaining aliquot was stored at the Planetary Geology Laboratory at Ohio University. All samples were analyzed using X-ray diffraction (XRD) to identify major minerals present. XRD spectra were collected over one hour/sample at Ohio University using a Rigaku Geigerflex X-ray diffractometer (40 kV, 30 mA). XRD spectra of breccia samples were compared to those of known mineral phases and geologic formations in the vicinity to determine whether the breccia consists of single or multiple geologic source units. A representative subset (24 samples, Table 1) was analyzed using X-ray fluorescence (XRF) to measure bulk chemistries. Samples were fused at 1050°C for two hours into disks and were analyzed by the heavy absorber fusion technique of Norrish and Hutton (1969). XRF analyses were used to compare the major element oxide chemistry of five of the breccia samples (Table 1) to those of known undisturbed geologic units collected in this study and to those (Table 2) reported by Rogers (1936), Lamborn and others (1938), Stout (1940), and Stout (1941). Comparisons were made using geochemical variation diagrams and by performing a Spearman's rank correlation coefficient analysis for SiO_2, Al_2O_3, Fe_2O_3(+FeO), MnO, MgO, and CaO. These major oxides were used because values were variable and all measured results were above the average detectibility limit of the XRF analyses (<0.01 wt. percentage). Thresholds for the correlation coefficient analysis were 90, 95, 99, 99.5 and 100 percent.

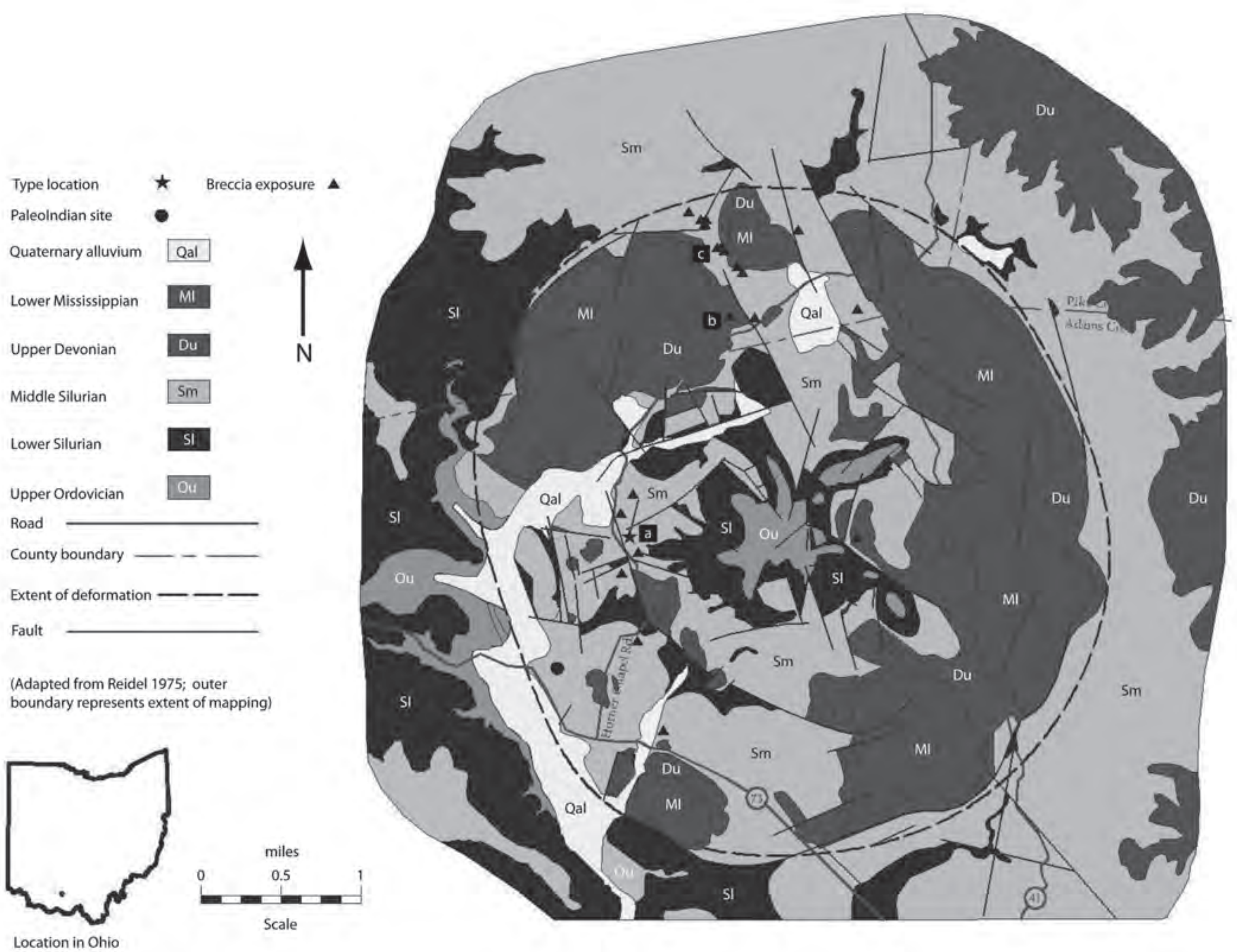


Figure 3. Geologic map of the Serpent Mound impact structure (after Reidel 1975), highlighting the type location (a) and two other sites where fining-upward sequences are exposed (b and c).

RESULTS

A total of 22 exposures of the breccia were located within the Serpent Mound impact structure (Fig. 3), all within the deformed area as defined by Reidel (1975) and only locally exposed as noted by Stout (1940) and Stout (1941). Twelve of the sites are situated within the transition zone, while the remaining sites are exposed in the ring graben in the northern part of the crater. Near the type location, the breccia is exposed over an area of over 20,000 m^2, but may be exposed over an area as large as 1.4 million m^2. Measured sections reveal that the anomalous breccia ranges from 3-21 m in minimum apparent thickness and ranges in elevation from 220-246 m above sea level. It is commonly situated adjacent to or near the Middle Silurian Peebles Dolomite or the Middle Silurian Lilley and Bisher Formations. In a few exposures in the northern ring graben, the Ohio Shale seems to be stratigraphically superposed upon the breccia.

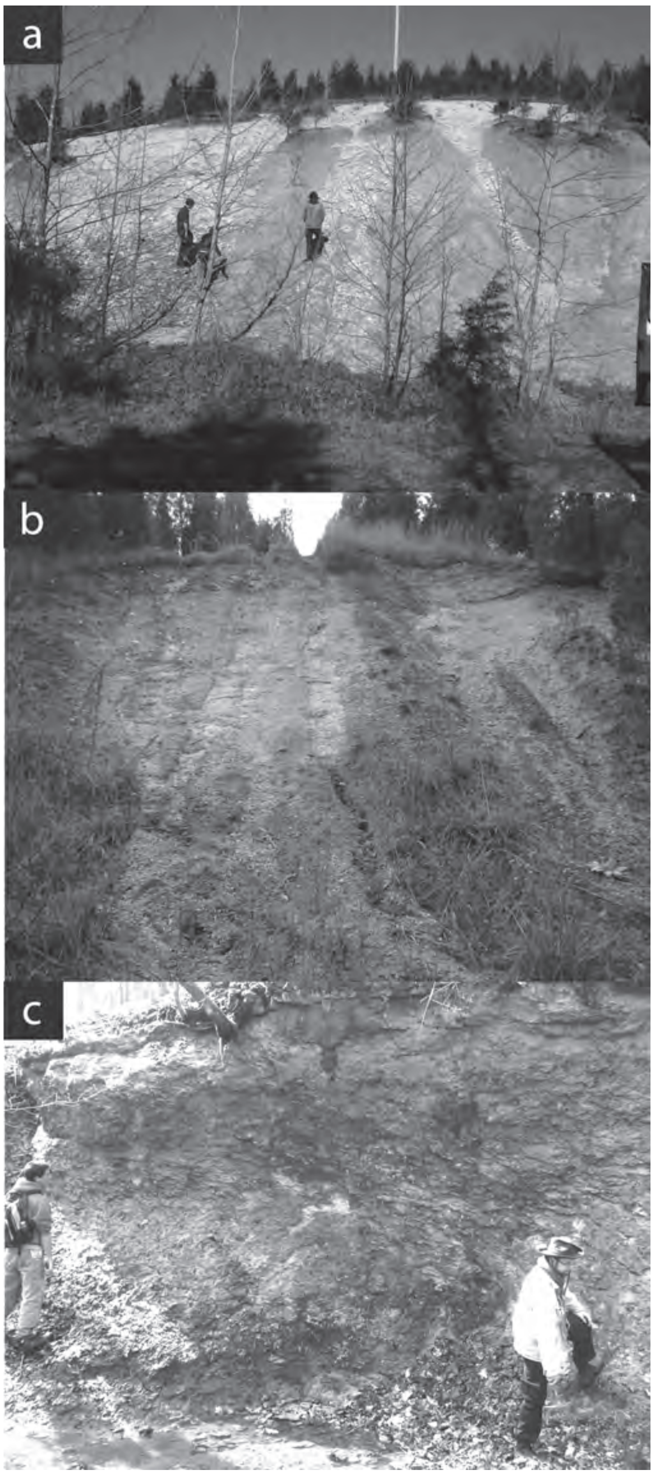


FIGURE 4. Breccia exposures at the type location (a) and in the northern part (b and c) of the crater. Locations are labeled on Figure 3.

XRD spectra ($2\theta = 20\text{-}80°$) of samples of undisturbed geologic units outside of the crater demonstrate characteristic mineralogical trends in the local stratigraphy (Table 3). Upper Ordovician-Lower Silurian rocks consist primarily of calcite and quartz, with lesser amounts of dolomite. Middle Silurian units are dominated by dolomite, whereas the Bisher and Lilley Formations have lesser amounts of quartz. The Lilley Formation also contains calcite in small amounts. Upper Devonian-Lower Mississippian units are all dominated by quartz.

Breccia samples consist of dolomite. Examination of XRD spectra ($2\theta = 20\text{-}80°$) of the 13 breccia samples reveals primary peaks at $2\theta \approx 31°$, 41.1°, 51.1°, and 50.6°, which correspond to dolomite. Sample SMB-9 is the only breccia sample that appears to contain minor amounts of quartz. Representative examples of breccia spectra are shown in Fig. 6.

XRF analyses show similar trends (Table 4). Upper Ordovician-Lower Silurian units that have a significant quartz component have characteristically higher weight percentage SiO_2 than other units dominated by carbonate minerals that have higher weight

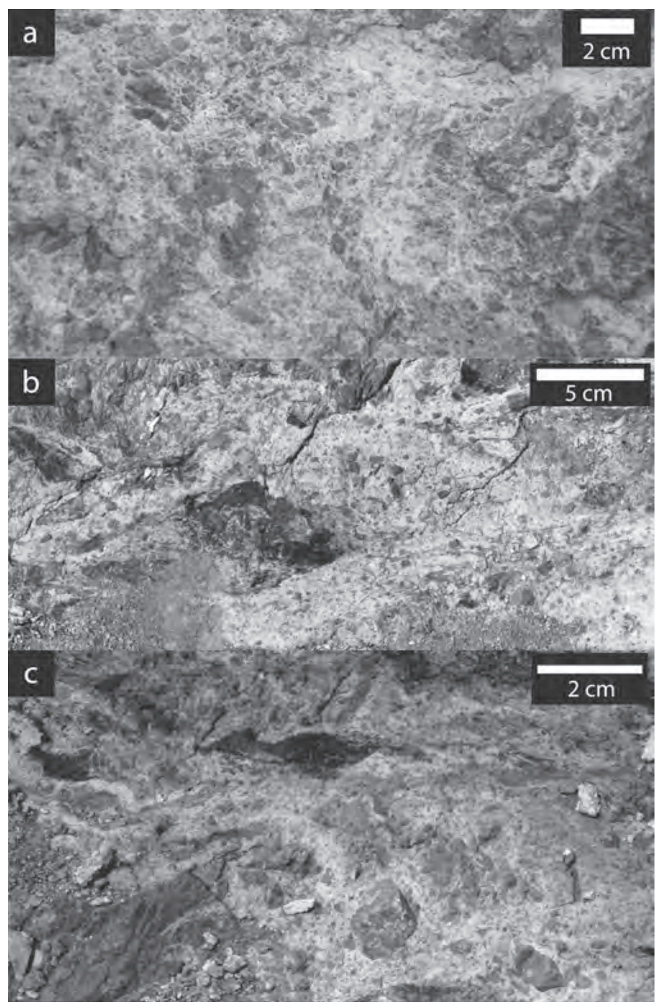


FIGURE 5. Field images of the anomalous breccia showing an apparent range of clast variety and clast/matrix ratios: (a) monomict, matrix-supported breccia, (b) polymict, matrix-supported breccia, and (c) polymict, clast-supported breccia. All three samples are from the type location shown in Figs. 3 and 4a.

percentages CaO and MgO (Table 4). Breccia samples also have very low weight percentages of SiO_2, but have relatively high values for CaO and MgO (Table 4). Representative geochemical variation diagrams are shown in Fig. 7 for visual comparison of the bulk compositions of breccia samples to known geologic units. Fig. 7 shows that weight percent oxides for the carbonate breccia are most closely associated with Silurian dolomitic formations, most specifically with the Middle Silurian Peebles and Upper Silurian Greenfield Dolomites. Statistical analyses (Table 5) indicate that the anomalous breccia is 95-100 percent correlated with the Peebles Dolomite, the Greenfield Dolomite, Tymochtee Formation, Lilley Formation, and Bisher Formation. The Brassfield Limestone and Drakes and Bull Fork Formations were correlated <90 to 99.5 percent, 90 percent, and ≤90 percent respectively. All other formations were correlated to the breccia at <90 percent.

DISCUSSION

The lateral extent and morphology of the breccia across the transition zone and the ring graben of the Serpent Mound impact structure suggest that the geologic process responsible for its deposition or emplacement was not restricted to a small area, but was rather associated with the crater and may have extended beyond its confines. The emplacement/depositional mechanism either operated during the Middle-Upper Silurian or only affected Middle-Upper Silurian carbonates. This is evidenced by the spatial association of the breccia with the Peebles Dolomite and the Lilley Formation, dolomitic composition of the breccia, and its close compositional correlation with Middle-Upper Silurian carbonates.

The spatial, mineralogical, and compositional association of the anomalous breccia with Middle-Upper Silurian carbonates is consistent with marine sediment deposition during the Middle-Late Silurian. The range of elevations over which the breccia is exposed (220-240 m above sea level) coincides with elevations of Middle Silurian carbonates (Table 2), when the eastwardly regional dip (Swinford 1985) is considered. Stratigraphic thickness, mineralogical, and compositional similarities between the breccia and the Middle-Upper Silurian Tymochtee Formation and Greenfield and Peebles Dolomites suggest that the breccia

Table 1

Samples collected for mineralogical and geochemical analyses. Unit descriptions may be found in Swinford (1985) and Shrake and others (2007).

Geologic Unit	Sample No.	Approximate Sample Location/Elevation	XRD	XRF
Berea Sandstone	BS-1	39˚1'14.00"N 83˚16'41.37"W/357m	x	
Bedford	BD-1	39˚1'15.20"N 83˚16'36.85"W/375m	x	
Ohio Shale	OS-1	39˚1'7.90"N 83˚17'24.62"W/293m	x	x
	OS-3	39˚1'7.90"N 83˚17'24.62"W/293m	x	x
Olentangy Shale	OL-1	38˚56'8.58"N 83˚21'21.76"W/228m	x	x
Tymochtee Dolomite	TY-1	38˚55'58.43"N 83˚21'53.31"W/244m	x	x
	TY-2	38˚26'25.55"N 83˚21'32"W/213m	x	x
Greenfield Dolomite	GN-1	38˚58'2.56"N 83˚20'14.44"W/227m	x	x
Peebles Dolomite	PB-1	38˚56'10.75"N 83˚26'46.70"W/280m	x	x
	PB-2	38˚56'10.75"N 83˚26'46.70"W/280m	x	x
	PB-3	38˚56'10.75"N 83˚26'46.70"W/280m	x	x
	PB-4	38˚56'20.41"N 83˚21'39.71"W/	x	x
Lilley Formation	LY-1	38˚56'12.24"N 83˚26'58.43"W/274m	x	x
	LY-1	38˚56'12.24"N 83˚26'58.43"W/274m	x	x
Bischer Formation	BH-1	38˚56'12.88"N 83˚27'3.37"W/267m	x	x
Estill Shale	ES-1	38˚56'13.44"N 83˚27'7.24"W/267m	x	x
	ES-2	38˚56'13.44"N 83˚27'7.24"W/267m	x	x
	ES-3	38˚56'13.44"N 83˚27'7.24"W/267m	x	x
Brassfield Formation	BL-1	38˚55'58.27"N 83˚27'53.81"W/197m	x	x
Drakes Formation	DK-1	38˚53'37.94"N 83˚27'11.38"W/201m	x	x
BullFork Formation	BF-1	38˚56'1.36"N 83˚28'41.75"W/199m	x	x
	BF-1	38˚56'1.36"N 83˚28'41.75"W/199m	x	x
Breccia	SMB-1	39˚2'2.34"N 83˚25'22.41"W/226m	x	
	SMB-1-1B	39˚2'2.34"N 83˚25'22.41"W/226m	x	x
	SMB-2	39˚1'45.20"N 83˚25'48.22"W/246m	x	x
	SMB-3A	39˚1'59.82"N 83˚25'47.94"W/220m	x	x
	SMB-4A	39˚2'12.52"N 83˚25'17.84"W/241m	x	x
	SMB-4B	39˚2'13.05"N 83˚25'16.77"W/235m	x	
	SMB-4C	39˚2'14.01"N 83˚25'16.12"W/226m	x	
	SMB-5A	39˚3'9.98"N 83˚24'28.69"W/220m	x	x
	SMB-5B	39˚3'9.98"N 83˚24'28.69"W/220m	x	
	SMB-6	39˚1'1.55"N 83˚25'5.23"W/219m	x	
	SMB-7	39˚1'29.26"N 83˚25'18.70"W/236m	x	
	SMB-9	39˚2'4.02"N 83˚25'57.97"W/256m	x	
	SMB-10	39˚2'4.02"N 83˚25'57.97"W/258m	x	

Table 2

Previous geochemical analyses of Geological Units Exposed in Southern Ohio and Northern Kentucky from [1]Lamborn and others (1938); [2]USGS Ohio Shale Analyses; [3]Stout (1941); [4]Rogers (1936); [5]Stout (1940); and †unpublished data from K. Milam

Formation	Sample	SiO_2	Al_2O_3	Fe_2O_3 (+FeO)	FeS_2	MgO	CaO	Na_2O	K_2O	CO_2	TiO_2	P_2O_5	SO_3 (S)	MnO	Ref.
Cuyahoga Formation	S1	64.2	15.7	7.1		1.6	0.5	0.5	3		1.1		0		1
Bedford Shale	S2	59.4	17.2	8.9		1.5	0.5	0.2	2.9		1.2		0		1
	S3	52.96	13.63	6.38		1.17	1.57	0.22	3.91		0.74	0.08		0.22	†
Ohio Shale	S4	49.28	12.27	9.34		1.54	1.05	0.38	3.35	1.01	0.71	0.11	5.35	0.042	2
	S5	63.03	16.56	5.62		1.56	1.1	0.4	4.05		0.88	0.1	1.16	0.06	1
Olentangy Shale	S6	63.11	16.57	5.12		1.17	0.98	0.52	4.44		0.96	0.11	1.47	0.01	1
	S7	0.4	0.02	0.26	0.09	21.55	30.16	*	*	47.25	0.01	0.08	0.05	0.03	3
	S8	1.65	0.02	0.38	0.06	20.95	29.68	0.12	0.16	46.51	0.04	0.05	0.02	0.015	3,4
Greenfield Dolomite	S9	1.77	0.04	0.51	0.03	20.62	30.29	0.01	0.01	46.62	0.02	0.03	*	0.02	4
	S10	3.1	0.03	0.43	0.19	20.51	29.2	0.1	0.11	45.65	0.06	0.17	0.03	0.03	4
	S11	0.44	0.14	0.25	0.06	21.6	30.1	0.01	0.03	47.29	0.01	0.05	0.01	0.03	3
	S12	0.92	0.12	0.9	0.15	21.15	29.55	0.02	0.07	46.74	0.02	0.06	0.01	0.06	3
	S13	0.33	0.09	0.42	0.02	21.07	30.75	*	*	47.07	0.02	0.05	0	0.08	3,4
Peebles Dolomite	S14	0.77	0.27	0.63	0.24	21.1	29.72	*	*	46.81	0.03	0.03	*	0.045	4
	S15	0.95	0.14	0.45	0.15	20.85	30.11	*	*	46.84	0.02	0.09	*	0.03	3,4
	S16	0.24	0.11	0.21	0.2	21.4	30.18	*	*	47.34	0.01	0.02	0	0.01	4
	S17	0.33	0.12	0.36	0.14	21.35	30.03	*	*	47.15	0.01	0.05	0	0.01	3,5
	S18	0.77	0.04	0.44	0.17	20.77	30.53	*	*	47.1	0.02	0.02	*	0.02	3,4
	S19	1.42	0.33	0.43	0.35	1.45	52.7	0.01	0.01	43.1	0.02	0.015	0.02	0.04	3,4
Lilley Formation	S20	7.01	1.64	1.09	0.14	19.08	27.17	0.16	0.12	42.47	0.09	0.04	0.14	0.05	3,4
	S21	6.68	1.78	0.99	0.27	18.94	27.23	0.11	0.14	42.35	0.11	0.02	0.08	0.02	3,4
	S22	13.4	1.8	2.88	0.63	16.52	24.47	0.1	0.11	38.5	0.14	0.05	0.08	0.06	3
	S23	18.38	3.92	1.99	0.33	12.8	25.75	*	*	35.4	0.22	0.07	0.04	0.07	3,4
Bisher Formation	S24	24.92	1.82	1.06	0.16	14.7	22.32	0.03	0.04	33.82	0.18	0.1	*	0.11	3,4
	S25	7.34	1.59	0.91	0.47	18.92	27.2	0.1	0.11	42.25	0.09	0.05	0.04	0.04	3,4
	S26	3.4	1.29	1.11	0.11	1.25	50.45	0.03	0.1	41.54	0.04	0.12	0.01	0.1	3
	S27	3.48	1.35	1.71	0.23	3.63	46.92	0.03	0.11	41.7	0.04	0.12	0.02	0.11	3
Brassfield Limestone	S28	7.41	1.55	1.9	0.25	2.7	45.44	0.15	0.25	39.27	0.14	0.16	0.02	0.15	3
	S29	4.5	1.29	2.69	0.3	2.07	47.45	0.03	0.04	40.38	0.07	0.21	*	0.22	3

Values for SrO, V_2O_5, BaO_2 and ZnO were * or not reported; C, H, H_20, and LOI values reported in most reference; * = values <0.01 weight percent may represent one or more of these formations. This is partially in contrast with field observations that initially indicated that the breccia may be a previously unidentified unit. For example, although the Peebles Dolomite is poorly bedded and does contain <1m thick breccia layers, it is unlike the breccia in that it has a characteristically vuggy texture, contains numerous macrofossils, and contains abundant asphalt (Swinford 1985; Baranoski and others 2003). Although much like the anomalous breccia, the Upper Silurian Greenfield Dolomite and Tymochtee Formation are noticeably devoid of macrofossils (Swinford 1985); bedding is well developed in the Greenfield and Tymochtee, but not the breccia. However, the lack of primary and secondary sedimentary features may be explained by extensive weathering, a notion that led previous geologists (Stout 1940; Stout 1941; Schmidt and others 1961) to identify the breccia as weathered Peebles Dolomite.

No evidence of fault movements such as strain indicators or slickensides has been observed in any breccia exposure. Furthermore, in contrast to fault breccias, which are concentrated in fault zones, the breccia is laterally extensive and exposed across the crater. The compositional homogeneity and lack of mineralogic diversity of the anomalous breccia do not support fault movements that could have transported fragments from a wider range of geologic units, such as the Upper Devonian Ohio Shale. In addition, no evidence of fault movements such as strain indicators or slickensides has been observed in any breccia exposure.

Compositional homogeneity of the breccia is also inconsistent with emplacement by post-impact gravitational collapse of over-steepened slopes with the impact crater. Slope failure would result in the entrainment and mixing of strata upslope from breccia exposures, which is in contrast to the XRD and XRF results. Collapse of the flanks of the central peak would result in mixtures of Upper Ordovician to Middle Silurian carbonates early on or later collapses that mixed Lower to Middle Silurian carbonates. In either case, final mineral assemblages would consist of calcite, dolomite, and quartz and breccia with higher weight percentages of CaO and SiO_2 than observed. Similarly, slope collapse in the northern ring graben [where there are numerous breccia exposures, would have incorporated quartz-rich strata of the Upper Devonian-Mississippian (Fig. 2), a notion not supported by our analyses (Table 3; Fig. 6)].

Deposition of brecciated material as ballistically-emplaced or resurged ejecta is also unlikely because of the compositional homogeneity. The concentration of the anomalous breccia within the crater and apparent lack of breccia outside the crater is consistent with fallback of ejecta and its removal beyond the crater rim or deposition by resurge following a marine impact event. However, the lack of mineralogic diversity or compositional heterogeneity suggests that the breccia does not represent approximately 480 m of excavated Upper Ordovician-Lower Mississippian strata (as calculated above). Such ejecta would be comprised of a dolomite-calcite-quartz mineral assemblage representing a mixture of carbonate and siliciclastic sedimentary rock. Even if the impact event occurred as recently as the Late Permian as suggested by Watts (2004) and Schedl (2006) and did not excavate Ordovician strata,

TABLE 3

Major minerals identified by XRD

Formation Name (Sample #'s)	Dolomite	Calcite	*Q*uartz
Berea Sandstone (BS-1)			x
Bedford Shale (BD-1)			x
Ohio Shale (OS-1, OS-3)			x
Olentangy Shale (OL-1)			x
Tymochtee Fm. (TY-1, TY-2)	x		x
Greenfield Dolomite (GN-1)	x		
Peebles Dolomite (PB-1 through 4)	x		
Lilley Formation (LY-1, LY-2)	x	x	x
Bisher Formation (BH-1)	x		x
Estill Shale (ES-1 through 3)	x		x
Brassfield Limestone (BL-1)		x	x
Drakes Formation (DK-1)	x	x	x
Bill Fork/Waynesville Fm. (BF 1,2)		x	x
Anomalous Breccia SMB-1 through SMB-10)	x		o

x = positive identification;
o = minor amount in sample SMB-9

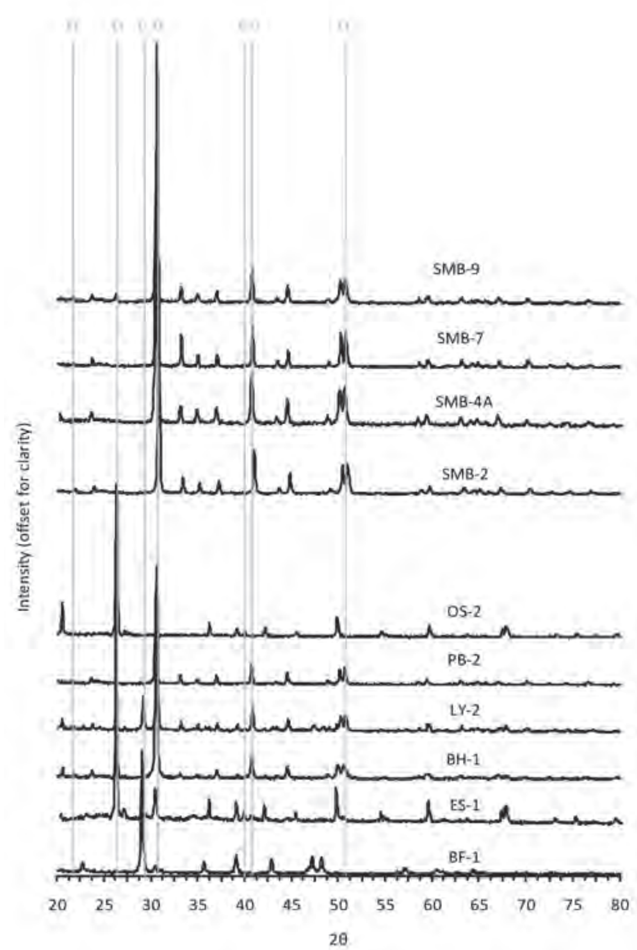
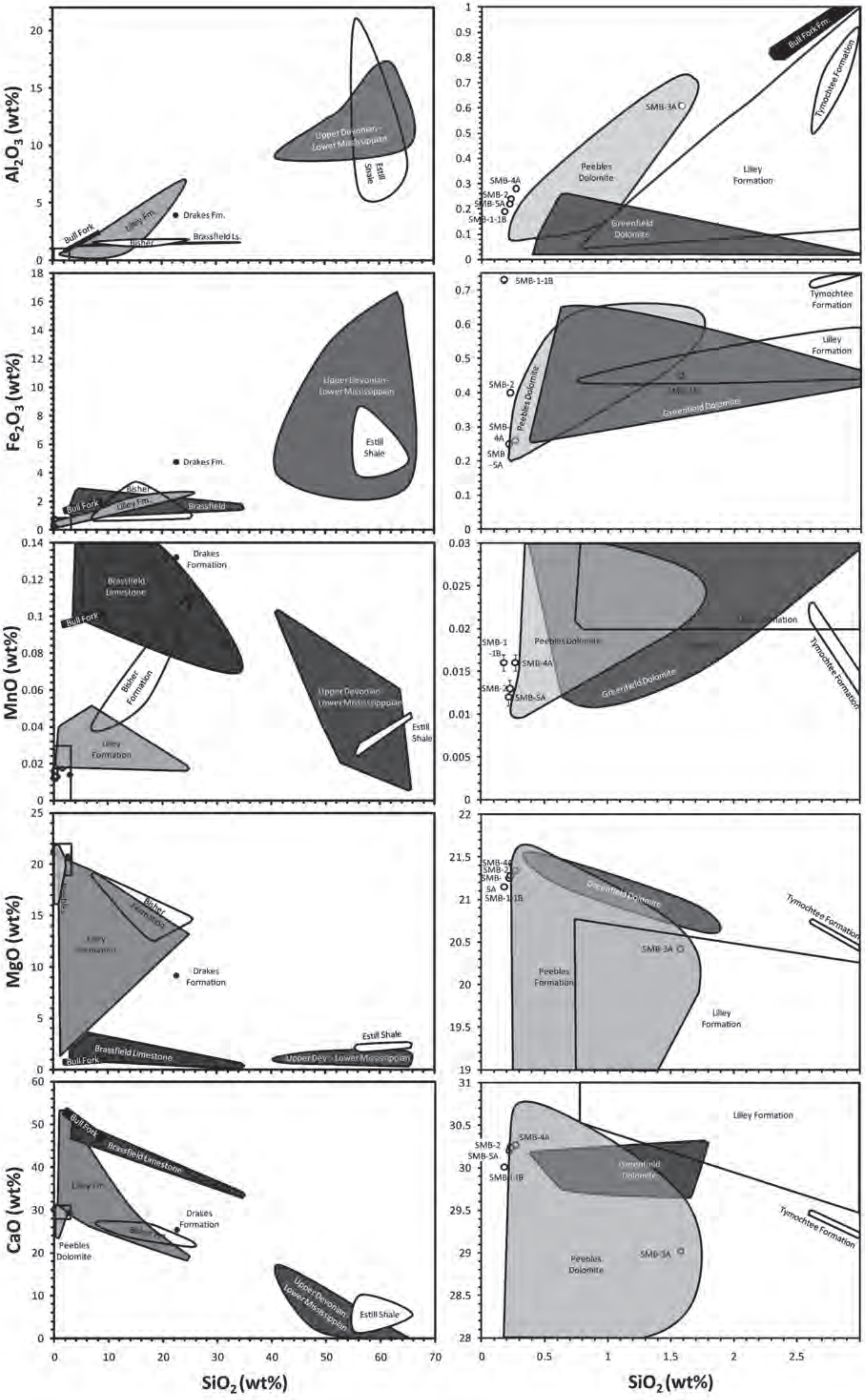


FIGURE 6. Representative XRD spectra of selected geologic units exposed near the Serpent Mound impact crater (lower) and the anomalous breccia (upper). Sample names correspond to those presented in Table 1. Excerpt for BF-1, all spectra have been offset for clarity. Gray vertical lines show some of the primary peaks for calcite (C), dolomite (D) and quartz (Q).



Al2O3 (wt%)
Fe2O3 (wt%)
MnO (wt%)
MgO (wt%)
CaO (wt%)
SiO2 (wt%)
SiO2 (wt%)
Upper Devonian-Lower Mississippian
Estill Shale
Drakes Fm.
Brassfield Ls.
Lilley Fm.
Bull Fork
Bisher
Brassfield
Drakes Formation
Brassfield Limestone
Bisher Formation
Lilley Formation
Peebles Dolomite
Bull Fork Fm.
Tymochtee Formation
Lilley Formation
Greenfield Dolomite
Peebles Formation
SMB-3A
SMB-4A
SMB-2
SMB-5A
SMB-1-1B
Estill Shale
Upper Dev. - Lower Mississippian

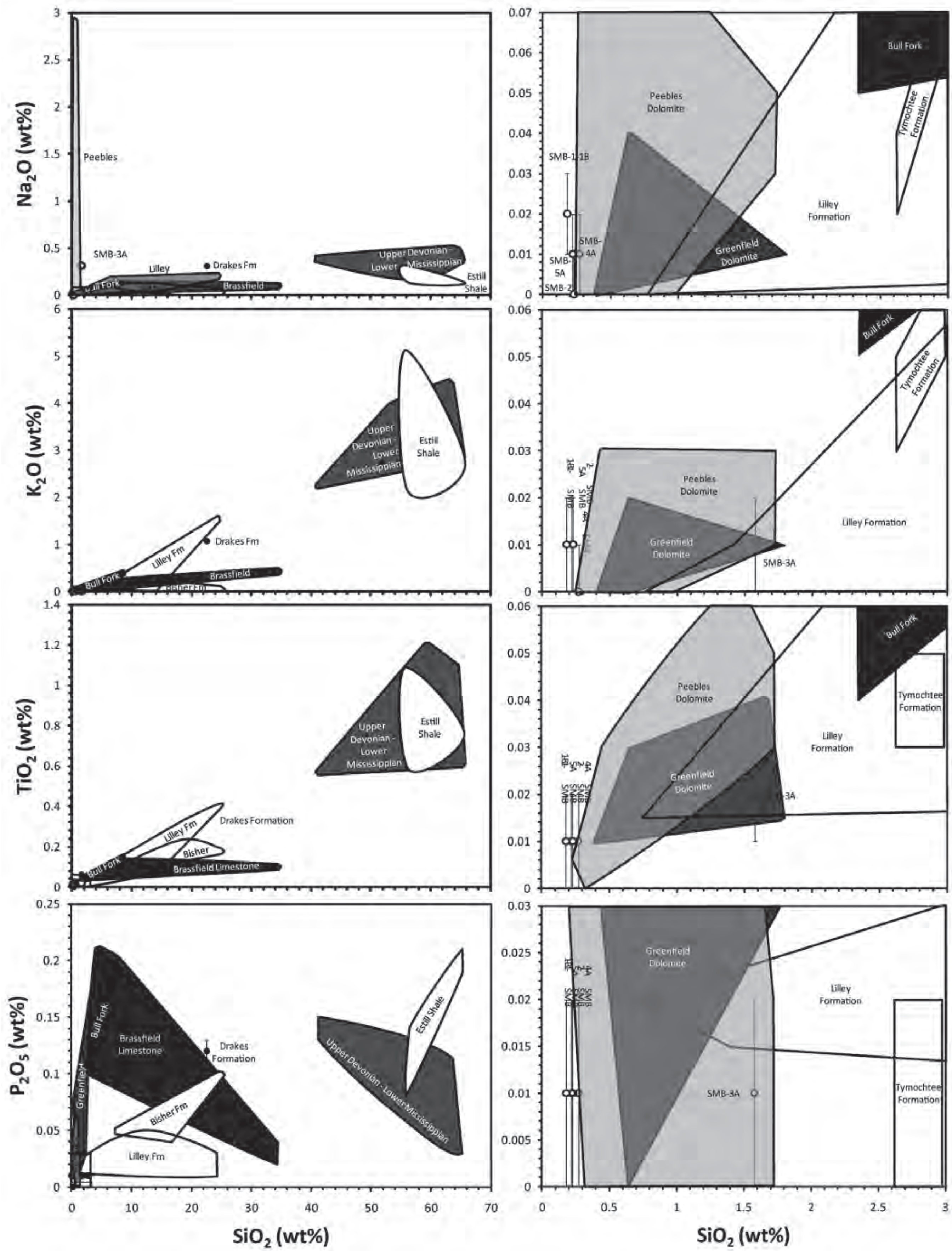


FIGURE 7. Geochemical variation diagrams of the anomalous breccia and geologic units exposed in Adams, Highland and Pike counties in southwestern Ohio. Compositional ranges for each geologic unit were constructed using data from Tables 2 and 4 (not including samples S19-S21 and S-25). Sample numbers correspond with those in Tables 1, 2 and 4. The left column shows the full range of analyses for a given oxide and the right column show an expanded view. Error bars shown where larger than the symbol for an individual sample.

ejecta from the event would have higher weight percentages SiO_2 compared to our results.

If the carbonate breccia represents ejecta, then it would require ejection of only up to 42 m (Swinford 1985) of Middle-Upper Silurian dolostones (Fig. 2), which is only one-tenth of that required for an eight km diameter impact crater. Such a notion would require a pre-Late Devonian impact (i.e. ejecta would not include the detrital sedimentary rock of the Devonian and Mississippian) because of the observed superposition of the Ohio Shale in the northern part of the crater. Under this scenario, the discrepancy in thicknesses might be explained by the erosional unconformity between the Upper Silurian Tymochtee Formation and the Upper Devonian Ohio Shale (Swinford 1985). Assuming that Upper Silurian and Lower to Middle Devonian strata were deposited in the southwestern part of the state (as in eastern Ohio), the combined thicknesses of these geologic units (Salina Group, Onondaga Limestone, etc.) with Middle-Upper Silurian strata at Serpent Mound could account for this discrepancy. However, the

Table 4

Major element (oxide) chemistry of geologic units and breccia samples (SMB) from X-ray fluorescence analyses.

Sample #*	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_2	Cr_2O_3	LOI	Total
OS-1	41.08	8.9	3.9	0.012	1	16.57	0.39	2.25	0.57	0.14	0.01	22.95	97.85
OS-2	52.96	13.63	6.38	0.22	1.17	1.57	0.22	3.91	0.74	0.08	0.01	18.08	98.77
OL-1	65.14	10.02	3.07	0.007	0.65	0.05	0.38	2.85	0.61	0.04	<0.01	17.42	100.2
TY-1	2.98	0.92	0.76	0.014	20.45	29.21	0.07	0.06	0.04	0.01	<0.01	45.77	100.3
TY-2	2.62	0.5	0.72	0.022	20.74	29.47	0.03	0.04	0.04	0.01	<0.01	46.22	100.4
GN-1	0.64	0.26	0.64	0.013	21.19	29.78	0.03	0.01	0.02	0.01	<0.01	46.51	99.11
PB-1	0.44	0.3	0.35	0.018	21.15	30.39	0.01	0.01	0.02	0.01	<0.01	47.57	100.3
PB-2	1.72	0.65	0.64	0.025	19.91	28.6	0.04	0.02	0.04	0.01	<0.01	48.51	100.2
PB-3	1.55	0.73	0.5	0.021	20.68	29.7	0.04	0.02	0.06	0.01	<0.01	46.79	100.1
PB-4	0.32	0.17	0.28	0.016	16.38	23.87	2.92	<0.01	<0.01	<0.01	<0.01	40.33	84.32
LY-1	24.29	7.02	2.65	0.018	13.26	18.96	0.2	1.54	0.4	0.02	<0.01	30.96	99.32
LY-2	14.02	0.93	1.99	0.035	13.94	29.67	0.07	0.09	0.1	0.04	<0.01	39.05	99.93
BH-1	16.74	1.22	3.02	0.055	14.35	26.42	0.05	0.13	0.18	0.05	<0.01	36.71	98.93
ES-1	65.31	8.39	4.99	0.046	2.42	5.54	0.14	2.63	0.76	0.02	0.01	9.27	99.69
ES-2	55.77	21.09	3.9	0.026	2.19	1.89	0.29	5.05	1.08	0.09	0.01	8.73	100.1
ES-3	56.47	5.89	8.68	0.03	1.97	9.57	0.16	2.05	0.59	0.13	<0.01	13.71	99.25
DK-1	22.57	3.94	4.77	0.132	9.15	25.32	0.31	1.07	0.33	0.12	<0.01	30.59	98.31
BL-1	34.43	1.64	1.62	0.07	0.37	33.57	0.01	0.44	0.1	0.03	<0.01	27.66	100
BF-1	2.34	0.81	1.39	0.096	0.74	52.48	0.06	0.06	0.05	0.11	<0.01	41.18	99.3
BF-2	8.46	2.43	1.97	0.101	0.98	46.93	0.12	0.38	0.15	0.19	<0.01	36.95	98.65
SMB-1-1B	0.18	0.19	0.73	0.016	21.15	30.01	0.02	0.01	0.01	0.01	<0.01	47.19	99.52
SMB-2	0.23	0.24	0.4	0.013	21.28	30.24	<0.01	0.01	0.01	0.01	<0.01	47.53	99.97
SMB-3A	1.58	0.61	0.45	0.018	20.42	29.02	0.31	0.01	0.02	0.01	<0.01	46.37	98.82
SMB-4A	0.27	0.28	0.26	0.016	21.34	30.27	0.01	<0.01	0.01	0.01	<0.01	47.7	100.2
SMB-5A	0.22	0.22	0.25	0.012	21.25	30.2	0.01	0.01	0.01	0.01	<0.01	47.65	99.85

* For geologic unit names, see Table 1.

Salina Group contains considerable halite, anhydrite, gypsum, and quartz (Pepper 1947; Frank 1963; Wolfe 2001), none of which were detected by XRD analyses of the anomalous breccia (Fig. 6).

Therefore, if the breccia represents ejecta, it would represent the ejection and deposition of *only* Middle-Upper Silurian dolostones prior to the Late Devonian deposition of the Ohio Shale. Such shallow excavation can occur with impacts into deeper marine settings (Gault and Sonnett 1982; Ormö and Lindström 2000), where larger amounts of water dissipate energy from the impact. The erosional unconformity at the Upper Silurian-Upper Devonian

TABLE 5

*Summary of Statistical Analysis Through Spearman's Rank Coefficient (percent correlated threshold met: * denotes <90 percent)*

Unit	Sample	SMB-1-1B	SMB-2	SMB-3A	SMB-4A	SMB-5A
Cuyahoga Formation	S1	*	*	*	*	*
Bedford Shale	S2	*	*	*	*	*
Ohio Shale	OS-1	*	*	*	*	*
	S3	*	*	*	*	*
	S4	*	*	*	*	*
Olentangy Shale	OL-1	*	*	*	*	*
	S5	*	*	*	*	*
	S6	*	*	*	*	*
Tymochtee Formation	TY-1	95	95	100	99.5	95
	TY-2	99	95	99.5	95	99
Greenfield Dolomite	GN-1	99	99	99	95	99.5
	S7	90	90	95	90	95
	S8	95	95	99.5	95	99
	S9	95	95	99.5	95	99
	S10	95	95	99	95	95
Peebles Dolomite	PB-1	95	95	99.5	95	99
	PB-2	95	95	100	99.5	99
	PB-3	95	95	100	99.5	99
	PB-4	95	95	99.5	90	99
	S11	95	95	99.5	95	99
	S12	95	95	99.5	95	99
	S13	99.5	99.5	95	95	99.5
	S14	95	95	99.5	95	99
	S15	95	95	99.5	95	99
	S16	95	95	99.5	95	99
	S17	99.5	99.5	95	95	99.5
Lilley Formation-Peebles Dolomite	S18	95	95	100	99.5	95
	S19	95	95	99.5	95	99
	S20	99.5	99.5	95	95	99.5
Lilley Formation	LY-1	*	*	95	90	*
	LY-2	90	90	99	90	90
	S21	95	95	99.5	95	99
	S22	95	95	99.5	95	99
	S23	95	95	100	99.5	95
	S24	95	95	100	99.5	95
Lilley-Bisher	S25	95	95	100	99.5	95
Bisher Formation	BH-1	90	90	99	90	90
	S26	95	95	99.5	95	99
	S27	90	90	99.5	95	90
	S28	*	*	95	90	*
	S29	95	95	100	99.5	95
Estill Formation	ES-1	*	*	*	*	*
	ES-2	*	*	*	*	*
	ES-3	*	*	*	*	*
Brassfield Limestone	BL-1	*	*	*	*	*
	S30	*	90	95	95	*
	S31	95	95	99.5	95	99
	S32	90	90	90	90	90
	S33	90	90	90	*	90
Drakes Fm.	DK-1	90	90	90	90	90
Bull Fork Formation	BF-1	*	*	90	*	*
	BF-2	*	*	90	90	*

and the occurrence of evaporites and certain sedimentary features in Upper Silurian carbonates (Treesh and Friedman 1974; Coogan, 1996; Tomastik 1997) however, indicates a regression following deposition of Upper Silurian carbonates in what is now southwestern Ohio.

If the breccia represents ejecta from a dry impact during the Late Silurian, the shallowness of the excavation would require that the collision must have occurred at a highly oblique impact angle. The asymmetric shape of the Serpent Mound impact crater (Reidel 1975) is consistent with this possibility. At the most common angle of 45° (Gilbert 1893; Shoemaker 1962) however, the shallow (<42 m) excavation required by the compositional homogeneity of the anomalous breccia would have been impossible. However, as impact angle decreases, so does crater depth (Gault and Wedekind 1978; Pierazzo and Melosh 2000). If the maximum possible excavation depth for the Serpent Mound impact event is 480 m and the anomalous breccia as potential ejecta requires only 42 m of excavation, then the amount of excavation represented by the breccia would be 8.75 percent of the maximum expected for Serpent Mound. We used final and maximum crater depths (Fig. 5 – along trajectory from Gault and Wedekind 1978) for impacts into dry pumice dust as a first order approximation of the percentage relationships between oblique and maximum (at a 90° impact angle) excavation depths. With this information, we calculated that the percentage of maximum possible crater depth (y) of an oblique impact is equal to:

$$18.099 \ln (x) + 13.3$$

where x represents the angle of impact. If y = 8.75%, then the required angle of impact for the Serpent Mound event would be approximately 0.78°, the probability of which is <3% (Gault and Wedekind 1978).

CONCLUSION

Field, laboratory, and statistical analyses all suggest that the anomalous breccia is a Middle-Upper Silurian dolostone member of the Tymochtee Formation, Greenfield Dolomite, Peebles Dolomite, or a mixture thereof. The lateral distribution and homogeneous dolomitic composition all support the conclusion that the anomalous breccia was deposited during the Middle-Late Silurian and was present at the time of the Serpent Mound impact event. This breccia was not formed by fault movements, slope collapse, or ejecta from the impact event. Further sedimentological and stratigraphic analysis, in the context of detailed geologic mapping, could provide insights into the formation of this pre-impact carbonate breccia and its stratigraphic significance.

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